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WADC TECHNICAL REPORT 52-5
SUPPLEMENT 1

HIGH-STRENGTH EPON LAMINATES

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SHELL DEVELOPMENT COMPANY

DECEMBER 1952

WRIGHT AIR DEVELOPMENT CENTER

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Shell Development Company

December 1952

Materials Laboratory
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Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

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FOREWORD

This report was prepared by Shell Development Company, under U. S. Air Force Contract No. AF 33(038)-19587, Supplement No. 1, Research and Development Order No. R614-12, "Structural Plastics", and covers work done between 1 January 1952 and 30 July 1952. Previous work under this contract was covered by WADC Technical Report No. 52-5. The work was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. A. Nahabedian acting as project engineer. Development work is being continued under an extension of the contract.

ABSTRACT

A laminate made from 181-114 glass fabric and EPON 1001 resin cured with dicyandiamide had a flexural strength of 76,900 psi at room temperature and 76,200 psi at 160°F (after 1/2 hour at 160°F). The compressive strength was 70,200 psi at room temperature.

With EPON laminates of this type, either boiling in water or aging at 95-100% relative humidity and 100°F for one hour caused a greater loss in strength than soaking for 30 days.

Improved Volan finish was the best of four new fabric finishes used in laminating with EPON 1001 and was the only finish better than 114.

Remarkably high strengths at elevated temperatures were obtained with an experimental resin known as EPON X-12100. Laminates made with this resin had a flexural strength above 60,000 psi at 392°F after 30 minutes at that temperature.

Liquid EPON resins 828 and 834 cured with dicyandiamide also produced laminates resistant to temperatures up to 300°F. After 1/2 hour at that temperature flexural strengths up to 44,000 psi were obtained. Aging for 200 hours at 300°F resulted in 52,900 psi flexural strength in one laminate. At higher temperatures, strengths fell off markedly.

Dimethyl cyanamide, a liquid curing agent, used with EPONS 828 and 834 produced laminates having up to 53,100 psi flexural strength at 392°F. This curing agent is toxic.

Flexural strengths at 300°F after 1/2 hour at 300°F up to 54,400 psi were obtained also in laminates made with mixtures of Plyophen 5015 (a phenolic resin) and EPON 1001, cured with dicyandiamide.

Of four large laminates 1/8" x 38" x 96" made with EPON 1001 at 25 psi, one was of excellent quality and another was considered good. There should be no difficulty in making EPON laminates of any large area.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDING GENERAL:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

TABLE OF CONTENTS

LIST OF TABLES

Physical Properties of a Laminate Containing EPON 1001

Various physical properties of a representative glass fabric laminate made with EPON 1001 were determined under Military Specification MIL-R-7575 (USAF).[a] Dicyandiamide, 4 phr,[b] was used as curing agent. The laminate was made from 16 plies of impregnated 181-114 superimposed with the grain of all plies parallel. The laminate was cured 5 minutes at contact pressure, followed by 25 minutes at 25 psi,[c] 330°F (165°C).

Complete physical data are set forth in Table 1. Outstanding properties include the following:

Flexural, ult., psi	76,900
Compressive, ult., psi	70,200
Flexural, ult., after soaking 30 days in water	71,300
" , at 160°F after 1/2 hour at 160°F	76,200

The burning rate (1.62 in/min) is greater than the allowable upper limit (1.0 in/min).

Effects of Water and Water Vapor

A study was made of the effects of boiling in water, of soaking in water at room temperature and of exposure to 95-100% relative humidity at 100°F on the flexural strength of laminates made from 181-114 glass fabric and EPON 1001 resin containing 4 phr of dicyandiamide. As shown by the following data, boiling for one hour is more severe than soaking for 30 days, and the latter is less severe than aging at 95-100% R.H. and 100°F for 30 days.

Boiling Time, Hours	Flex., Ult., psi
0	77,500
1	61,700
2	58,200
3	52,600

Aging Time, Days	Flex., Ult., psi, After Soaking	100°F, 95-100% R.H.
0	77,500	77,500
10	75,800	72,200
20	72,700	60,900
30	64,800	56,200
60		52,900

a) Testing under Spec. 12049 was substantially completed before issuance of superseding Spec. MIL-R-7575. All tests for which data are presented in this report were made according to LP-406A.
b) "phr" as used throughout this report means parts per hundred of resin.
c) All laminates for which data are presented in this report were cured at 25 psi.

The laminate used in the foregoing test was cured 5 minutes at contact pressure, followed by 25 minutes at 25 psi, 330°F (165°C).

Use of New Glass Fabric Finishes

Four new fabric finishes were investigated for use in EPON laminates. Strengths obtained with three of the finishes were lower than strengths obtainable with 114 finish. One of the three, in a previous study, had tested much higher in flexure, making the validity of the data questionable. The fourth new finish, "Improved Volan," gave exceptionally high flexural strengths but was low in compressive strength. Unfortunately, the new fabrics were received too late to permit repeating the study in time for this report, although further work is in process.

Complete data are presented in Table 2. For convenience, some of the more important data are outlined below:

	Flexural, ult., psi		
Finish	Initial	After Soaking 30 Days	Compressive, Ult., psi
114	76,900	71,300	70,200
Improved Volan	81,700	76,000	57,400
136	67,800	60,500	62,400
Linde	62,500	58,200	57,400
Garan-RS 49	63,900	52,500	55,800

Data relating to Finish 114 were obtained on a 16-ply laminate. Similar data are being determined on a 12-ply laminate. Twelve-ply laminates were used for the other finishes.

It is interesting to note that in the production of the above Volan, 136 and Linde laminates, pieces of fabric about 3 yards long were spliced together and impregnated by machine in one pass using a dip tank containing one batch of EPON resin solution. The resin contents of the impregnated fabrics after drying were:

Finish	% Resin
Volan	40
136	45
Linde	36

A similar laminate made with 181 glass fabric containing a benzoato chromic chloride finish had an initial flexural strength of 77,900 psi, which dropped to 68,500 psi on soaking for 30 days.

Laminates Containing EPON X-12100

A new experimental resin known as EPON X-12100 was examined for use in glass fabric laminates. This resin is a low melting solid, which is dissolved in acetone for impregnation. Dicyandiamide, which is used as the curing agent, is first dissolved in a hot mixture of twice its weight of water plus thrice its weight of acetone. The hot dicyandiamide solution is added slowly to the EPON solution with vigorous stirring. Fabric is impregnated with this solution and dried 10 to 20 minutes at about 200°F before being used in laminating.

Because of lack of time, the study of this new resin did not progress appreciably beyond the preliminary stages of seeking the optimum dicyandiamide concentration and optimum curing conditions. It was found that laminates cured at a constant platen temperature of either 275° or 330°F (135° or 165°C) were less strong than laminates cured initially at 275°F, followed by 330°F to complete the cure.

A laminate from EPON X-12100, containing 4 phr dicyandiamide, cured under conditions which have become standard for EPON 1001 (5 minutes at contact pressure, followed by 25 minutes at 25 psi, 330 °F), had a flexural strength of only 38,000 psi, compared to 74,000-77,000 psi obtainable with EPON 1001. From the lack of flash and high resin content of EPON X-12100 laminates maintained at 330°F for the entire cure period, it appears that this resin cures more rapidly than EPON 1001. This belief is supported by the improvement in initial flexural strength resulting from curing for 10 minutes at 275°F, followed by 20 minutes at 330°F. Precuring for 5 minutes appeared optimum. Strengths up to 74,700 psi were obtained.

An outstanding characteristic of laminates from EPON X-12100 is their high strength at 300°F and 392°F. At 300°F after 1/2 hour at that temperature flexural strengths of 34,000 psi or more were obtained and four laminates had flexural strengths greater than 40,000 psi. Laminates maintained at 300°F for 200 hours became even stronger, averaging about 56,000 psi, with one high value of 64,600 psi. At 392°F, after 1/2 hour at that temperature, flexural strengths became more variable. Laminates containing 4 phr of dicyandiamide, cured for 30 minutes, varied in flexural strength at 392°F from 3,800 to 36,200. Prolonging the press cure to one hour raised the flexural strength at 392°F to 54,900 in one instance. Increasing the concentration of curing agent to 6 and 8 phr resulted in even greater improvement (61,100 to 61,900 psi) at 392°F in laminates cured only 30 minutes.

Data so far obtained on laminates from EPON X-12100 are presented in Table 3. The table is spotty because effort was shifted to other EPON laminating problems shortly after the inception of work on EPON X-12100. There are also certain unexplained variations in test data which can be resolved only by further investigation.

Most apparent deficiency of EPON X-12100 laminates is their relatively poor resistance to water. After soaking for 30 days, flexural strengths ranged from 18,000 to 47,000 for 181-114 fabric laminates cured 30 minutes. Doubling the cure time increased strength after soaking to 54,700 in one instance. It is expected that one or more of the new finishes may effect considerable improvement of this property. Laminates made with 181-BJY tested at 51,700 to 58,500 psi flexural after soaking.

Laminates from Liquid EPON Resins Cured with Dicyandiamide

Liquid EPON resins 828 and 834[a] are customarily cured with liquid amines. Dicyandiamide, which is very effective in curing solid EPON resins (which are applied to the fabric from solution), is insoluble in liquid EPONS and must be added as a solution in another liquid or must be intimately mixed with the EPONS by ball-milling or the like. Fabric impregnated with a solution containing a volatile solvent must be dried before laminating.

Laminates from liquid EPON resins cured with dicyandiamide have shown promising high-temperature resistance. At 150°C after 1/2 hour at that temperature, flexural values up to 44,000 psi have been obtained. After 200 hours at 300°F, the only laminate tested under these conditions had 52,900 psi flexural strength. At 392°F, however, strengths dropped off markedly. The greatest strength recorded at 392°F was 14,000 psi. Strengths after soaking for 30 days were generally good (up to 63,300 psi) as were initial flexural strengths (up to 75,700 psi).

Present indications are that excellent strengths under all conditions except 392°F can be obtained from EPON 828 cured with either 4 or 8 phr of dicyandiamide at 329°F.[b] Curing for one hour with 4 phr of curing agent is about equivalent to curing 30 minutes with 8 phr, and even greater strengths can be obtained by using a one-hour cure with the larger amount of curing agent. Typical data follow:

Daily phr	Cure[c]	Initial	After Soaking	At 300°F	At 392°F
4	5/55/329	75,700	59,900	38,000	14,000
8	5/25/329	73,900	58,600	30,400	13,200
8	5/55/329	73,100	63,300	44,000	14,000

More complete data are presented in Table 4.

a) EPON 828 was formerly EPON RN 48.
EPON 834 was formerly EPON RN 34.
b) Including a 5-minute precure.
c) A simple system of designating curing conditions is used throughout this report. In each group of three numbers separated by diagonal lines, the first number designates the number of minutes at contact pressure, the second designates the number of minutes at 25 psi, and the third designates temperature in degrees F. Attention is called to the change from the Centigrade scale, which was used in previous reports.

Laminates Containing EPON/Phenolic Resin Mixtures

Phenolic resins were added to EPON resins with the intention of providing additional cross-linking, thereby improving hardness and strength at elevated temperatures.

In the initial work on each EPON/phenolic resin system, 3" x 3" laminates were made from 6 plies of 181-114 glass cloth, cured between cellophane in a press, removed while hot and placed beneath a flat steel block for cooling. As much cellophane as could be readily removed was stripped off, but no attempt was made to remove any single layer which adhered tightly to the laminate. Five Barcol impressions were made at spaced points on each side of the laminate. The average of the ten values was considered the Barcol hardness.

Laminates so made from EPON 1001 containing 4 phr dicyandiamide, cured 5/5/329, had a Barcol hardness of 57 to 63.

EPON/phenolic resin systems which appeared promising on the basis of the foregoing tests were then used in preparing larger laminates for strength measurements. Such laminates were cooled in the press to insure flatness.

Ten phenolic resins were examined as additives for EPON resins in laminating. Experience with each resin is discussed separately below. In all instances, the EPON component is given first in resin ratios and such ratios refer to solids only. Curing agent concentrations are based on the total solids content of each mixture, including both EPON and phenolic solids.

Bakelite 15100. (Eighty-three per cent solids by determination in these laboratories) Used with EPON 1001 only. Cured with 4 phr dicyandiamide.

Ratio	Cure	Barcol
50/50	5/5/329	2
90/10	"	9

Super-Beckacite 3011. Assumed 100% solids. Used with EPON 1001. 4 phr dicyandiamide was used as curing agent.

Ratio	Cure	Barcol
50/50	5/5/329	42
70/30	5/5/329	5
90/10	1/9/329	56

This resin was also mixed with EPON 828 and cured with 5 phr of DMP-30 as the tri (2-ethyl-hexoate).

Ratio	Cure	Barcol
70/30	0/10/239	51
"	0/20/239	55
"	0/10/239	57

General Electric R-108. Mixtures of 25 parts of R-108 with 75 parts of EPON 1001, 1007 or 1009 in acetone solution were catalyzed with 0.5, 1 and 1.5 phr of phosphoric acid. Laminates were cured at 275° and 329°F. Most of the cures were limited to 10 minutes, but several cures were extended to 30 minutes. The hardness of all laminates was low. The highest Barcol was 41, obtained on a laminate made from EPON 1007 and 0.5 phr phosphoric acid. A full-size laminate containing this system, cured 3/27/329, had 49,000 psi flexural strength.

Another series of laminates was made from mixtures of EPON 1001 and R-108, using 90/10, 70/30 and 50/50 ratios with 2, 4 and 8 phr of dicyandiamide as curing agent. A high Barcol hardness of 66 was obtained with the 90/10 formulation, cured with 4 phr of dicyandiamide. The 70/30 formulation gave a maximum of 59 Barcol. No hard laminates were obtained when the EPON/phenolic ratio was decreased to 50/50.

A laminate from EPON 1001 and R-108 in 90/10 ratio, cured with 4 phr dicyandiamide 3/27/329 tested in flexure as follows:

Initial	77,800 psi
After boiling 3 hours	55,600
After soaking 30 days	69,900
At 300°F after 1/2 hour	6,300

Attempts were made to cure 50/50 mixtures of EPON 1001 and R-108 with 5 phr of DMP-30 added as the tri (2-ethyl hexoate). Cures at 239 and 329°F failed to yield laminates which registered on the scale of the Barcol impressor.

Resimene P-97. (Fifty per cent solids) Used only with EPON 1001. Dicyandiamide was employed in three concentrations.

Ratio	Dicy., phr	Cure	Barcol
90/10	4	1/9/329	64
"	"	2/8/329	64
"	"	3/7/329	38
70/30	4	0/10/329	49
"	"	1/9/329	65
"	"	2/8/329	34
50/50	2	0/10/329	40
"	"	1/9/329	66
"	"	5/5/329	2
"	4	0/10/329	47
"	"	1/9/329	58
"	"	2/8/329	22
"	8	0/10/329	51
"	"	1/9/329	61
"	"	2/8/329	38

Test data on laminates made with this system of resins is given in Table 5. Three of the laminates exhibited an apparent increase in strength after soaking in water for 30 days.

Bakelite BV9700. (73% solids as determined in these laboratories) The following exploratory tests were performed. No added curing agent was used. The EPON resin was 1001.

Cure	0/100	Barcols with Indicated Resin Ratio 50/50	70/30	90/10
5/5/275	22	30	30	0
5/25/275	29	42	48	15
0/10/329	51	42	15	2
0/30/329	56	49	8	33
2/8/329	15	24	43	11
2/28/329	15	26	57	20
5/5/329	8	5	1	9
5/25/329	12	6	3	10

A laminate containing a 70/30 mixture of these resins tested at 45,900 psi initial flexural; 10,000 psi at 300°F after 1/2 hour at 300°F.

Bakelite BR 7095. (100% solids) Used with EPON 1001 without added curing agent.

Cure	0/100	Barcol with Indicated Resin Ratio 50/50	70/30	90/10
0/10/329	-	23	20	20
2/8/275	37	38	27	23
2/28/275	39	35	27	30
5/5/275	8	16	0	1
5/25/275	3	16	4	10

Plyophen 5023. (Assumed 100% solids) Used alone with 1 phr phosphoric acid.

Cure	Barcol
1/9/275	36
1/29/275	43
2/8/275	27
2/28/275	38
5/5/275	0
5/5/275	1
0/10/329	25
1/9/329	15

Mixed with EPON 1001 in several ratios and cured with 1 phr phosphoric acid, the following Barcols were achieved.

Cure	Barcols with Indicated Resin Ratio 50/50	70/30	90/10
1/29/275	15	0	0
1/9/329	16	27	0
1/29/329	24	0	0

With 4 phr of dicyandiamide in place of the acid in the above system, Barcols were as follows:

2/8/329	0	0	20
5/5/329	5	0	1

In the absence of any curing agent, the highest Barcol obtained after 30 minutes curing at 275 or 329°F was 5.

Plyophen 5023 was used with EPON 1009 without added curing agent with the following results:

Cure	Barcols with Indicated Resin Ratio 50/50	70/30	90/10
5/5/275	21	3	0
5/25/275	25	2	0
0/10/329	27	18	4
5/5/329	47	44	24

Durez 13263. 100% solids. So many preliminary laminates were made with this resin in combination with EPONS 1001 and 1007 that it would be impracticable to delineate all of them. Highest Barcols were obtained with 90/10 and 70/30 ratios, using 4 phr dicyandiamide, curing 1/9/329. With the 50/50 ratio, Barcols were improved by reducing the dicyandiamide concentration to 2 phr and by curing at 275.

Flexural strengths of larger laminates follow:

EPON/phenolic resin ratio	50/50	90/10	90/10
Cure	2/28/275	1/29/329	5/25/329
Flexural, ult., psi			
Initial	59,000	73,600	34,000
After boiling 3 hours			17,500
After soaking 30 days			31,000
At 300°F after 1/2 hour		5,200	4,400

Plyophen 6000. 70% solids. Used with EPONS 1001 and 1009 without curing agent, as follows:

Cure	Barcols with Indicated Resin Ratio EPON 1001 50/50	70/30	90/10	EPON 1009 90/10
5/5/275	13	2	0	21
5/25/275	16	2	24	33
0/10/329	27	47	-	9
2/8/329	6	18	8	36
5/5/329	8	0	0	7
5/25/329	11	1	0	24

Plyophen 5015. 70% solids. By itself, without added curing agent, this resin made very satisfactory laminates:

Cure	Barcol
2/8/275	60
0/10/329	52
2/8/329	5
2/8/239 0/20/329	35

In blends with equal parts of EPON 1001, the optimum concentration of dicyandiamide appeared to depend on curing conditions.

Cure	Barcols with Indicated Concentrations of Dicyandiamide 0	2	4
2/8/275	24	43	45
0/10/329	30	38	40
2/8/329	39	3	8
2/8/239	0	0	0
2/20/239	27	50	64

At the 70/30 resin ratio, the following Barcols were obtained:

Cure	Barcol with Indicated Concentration of Dicyandiamide 0	2	4	8
2/8/275	27	40	51	60
2/28/275	41	52	57	60
0/10/329	29	44	40	60
1/9/329	53	62	48	28
2/8/329	7	1	9	23

A similar series was run with the 90/10 ratio.

2/8/275	25	49	54	52
2/28/275	42	49	48	47
0/10/329	39	47	52	57
1/9/329	57	39	36	70
2/8/329	4	5	2	8

Flexural strength data are set forth in Table 6. Compressive strengths as high as 55,900 psi were obtained using long specimens held in a jig. Strengths at 300°F after 1/2 hour at 300°F were several times greater than strengths obtained with EPON 1001 without a modifier. Plyophen 5015 alone, cured without added curing agent, tested at 52,700 psi initial flexural: 47,100 psi at 300°F after 1/2 hour at 300°F. Laminates containing this resin tend to be porous, apparently due to condensation water.

Strengths at Elevated Temperatures

The elevated temperature properties of laminates made with the following three resins are discussed fully in separate sections of this report devoted to those resins:

EPON X-12100
EPON/phenolic resin mixtures
Liquid EPON resins

In addition to the foregoing, laminates representing a variety of different EPON resin formulations and curing conditions were subjected to flexural testing at 300°F after 1/2 hour and after 200 hours at that temperature. In most cases, material remaining from previously prepared laminates was utilized. Data so obtained are presented in Table 7 together with room temperature flexural strengths. Blanks in the table are due to an insufficiency of material for all tests.

All of the high-temperature strengths given in the table are low in comparison with those obtainable with the 3 resin systems listed above.

Curing with Cyanamide and Dimethyl Cyanamide

Cyanamide is the monomeric form of dicyandiamide, the latter being a very effective curing agent for EPON resins. In highly exploratory tests, a sample of cyanamide (purchased as such from Eastman Kodak Company) did not cure EPON 1001 as effectively as dicyandiamide in the one concentration employed (4 phr). The compound was dissolved in acetone and water and used in accordance with the technique employed with dicyandiamide. Impregnated 181-114 glass fabric was dried 10 minutes at 200°F and used in making 6 ply 3" x 3" laminates, which were cured as indicated, cooled to room temperature and tested for hardness.

Curing Conditions	Barcol
5/5/275	3
0/10/329	9
2/8/329	35
5/5/329	5

A similar laminate made with EPON 1001 and 4 phr of dicyandiamide, cured 5/5/329, had a Barcol hardness of 63.

Dimethyl cyanamide is a liquid relative of dicyandiamide which mixes readily with EPON. Mixtures of cyanamide with EPON resin have an indefinitely long pot life at temperatures at least up to 122°F. The obvious advantage of using this compound as a curing agent motivated the following investigation:

Two glass cloth laminates were made from EPON 828 containing 5 phr of dimethyl cyanamide using slightly different curing conditions. Another was made similarly with 8 phr of dimethyl cyanamide. The smaller amount produced the stronger laminates. A fourth laminate, made from EPON 834, was almost identical in strength to the best laminate made from EPON 828 with this curing agent. Strengths at 392°F were above 50,000 psi flexural--exceptionally high and previously obtainable only with EPON X-12100.

The following data relate to laminates from 181-114 glass fabric cured 30 minutes at 330°F.

EPON Resin	Curing Agent phr	% Resin	Precure, min.	Flexural, ult., psi At Rm. Temp.	Flexural, ult., psi At 392°F
828	5	28	5	70,000	53,100
"	5	28	10	62,600	
"	8	28	10	58,400	
834	5	27	10	69,900	51,600

Attempts to use dimethyl cyanamide as a curing agent for solid EPON resins such as EPON 1001, were unsuccessful, presumably because of volatilization of the compound during drying of the impregnated cloth to remove solvent.

Dimethyl cyanamide is extremely toxic.

Laminates of Large Area

Several laminates 1/8" x 38" x 96" were made from 181-114 glass fabric impregnated with EPON 1001 containing 4 phr of dicyandiamide. The laminates were pressed in contact with stainless steel cauls which had been coated with Dow Coming Release Agent XE 135A. To protect the cauls from damage and to compensate for any unevenness in the faces of the press platens, one or two plies of .060" alpha-allulose sheet were employed between each caul and the adjacent press platen.

In making the first laminate, the 50" x 100" press presented a problem; the automatic pumping unit could not be made to operate at below 100 tons pressure (46 tons pressure gives 25 psi on a 38" x 96" laminate). It was thought possible to approximate the required pressure by starting and stopping the pump manually, but during the curing of the laminate actual pressure variations were appreciable. The laminate was cured 15 minutes at contact pressure, followed by 25 minutes under pressure at 329°F, followed by cooling in the press under pressure. Presumably because of pressure variations, the laminate was non-uniform and badly pitted.

The press was then provided with an auxiliary low pressure pump and low pressure guage. With this new equipment it became possible to apply and maintain with substantially no variation any desired pressure below 100 tons. A second laminate made using the curing conditions attempted for the first laminate was much improved over the first, but contained high and low-resin spots due to uneven impregnation. A third laminate made similarly with more evenly impregnated cloth had an excellent appearance over most of its area, but contained a few imperfections due to wrinkles present in the impregnated cloth prior to laminating. A fourth laminate made similarly with freshly-impregnated cloth had an excessive amount of flash and was porous in texture. The cause of the poor quality of this laminate has not been determined. Imperfect drying of the impregnated cloth with resultant entrapment of acetone is a possible cause.

In view of the excellence of the third laminate, it is felt that there should be no difficulty in working out conditions for the production of essentially perfect EPON laminates of large area.

<u>Sample Laminates</u>

To fulfill contract requirements, numerous laminates were prepared from liquid and solid EPON resin and shipped to the Wright Air Development Center for evaluation.

Considerable difficulty was encountered in making thick laminates for this shipment from EPON 828 and DMP-30 tri (2-ethyl hexoate). When the resin was used at room temperature, its viscosity was so great that air in objectionable amounts was entrapped in the laminate. When the resin was warmed to reduce its viscosity, gelation sometimes occurred before a thick lay-up could be completed. The procedure which was developed after repeated experimentation consisted in floating individual plies of preheated glass fabric on the surface of catalyzed EPON 828 heated to 50-55°C (122-131°F) until the resin penetrated to the upper surface of the fabric, then pushing the impregnated ply to the bottom of the bath of resin and repeating the process with another ply. In this way laminates were laid up beneath the surface of the hot resin and subsequently were removed from the bath, sandwiched between Teflon film (release agent) and laminated in a press. By working rapidly, it was possible to complete a 10" x 10" 48-ply lay-up before the resin gelled.

Fillers

The addition of finely divided fillers to polyester resins is common practice in molding and laminating. Fillers function chiefly as extenders, reducing cost appreciably on a weight basis and more moderately on a volume basis. They further reduce shrinkage and improve surface finish.

With the aim of determining the usefulness of fillers in EPON laminates, ten finely divided substances were mixed with EPON 828 containing DMP-30 tri (2-ethyl hexoate) as curing agent and used in laminating with 181-114 glass fabric. Quantities were selected to produce laminates containing approximately 5% and 15% of the filler based on the total weight of the laminate. (Two of the fillers, Hi Sil and Silene EF, resulted in such viscous mixtures with EPON 828 that only the smaller amount could be used.)

All of the fillers caused a significant decrease in the flexural strength of the laminates, as shown by the data in Table 8.

Nylon and Dacron Reinforcement

To satisy contractural requirements, laminates were made with EPON resin using nylon and Dacron fabrics in place of glass fabric. Since no commercial source of the fabrics suggested by the Wright Air Development Center could be located, fabrics having the following description were used:

Supplier	Deering Milliken	Burlington Mills	Burlington Mills
Fiber	Orlon	Orlon	Dacron
Code	D-2401	34-86	34-33
Weave	Plain	Basket	Basket
Warp threads/in.	68	50	51
Fill threads/in.	38	52	44
No. of plies (yarn)	2	2	2
Denier	200	200	250
Weight, oz/yd^2	5	5.5-6.1	6.5-7.0

Laminates were made from 12 plies of each of the orlon fabrics and 9 plies of the Dacron fabric impregnated with EPON 1001 containing 4 phr dicyandiamide. Standard curing conditions were used (5/25/329, 25 psi). The areas of the cured laminates were less than that of the superimposed plies before curing as a result of shrinkage of the fabric. Based on reduction in area, shrinkage occurred as follows:

Fabric	Shrinkage
Orlon D-2401	3%
Orlon 34-86	20
Dacron 34-33	24

Less shrinkage would be expected in using these fabrics with EPONS 828 or 834 cured with DMP-30 tri (2-ethyl hexoate) or the like, because of the lower curing temperatures employed.

Table 1. PHYSICAL PROPERTIES OF A LAMINATE MADE FROM 181-114 GLASS FABRIC IMPREGNATED WITH EPON 1001 CONTAINING 4 PHR OF DICYANDIAMIDE

Flexural, ult., psi.	76,900
mod., x 10^{-6}	3.72
yield, psi	69,600
Tensile, ult., psi	55,300
mod., x 10^{-6}	3.52
yield, psi	55,300
Compressive, ult., psi	70,200
mod., x 10^{-6}	4.26
yield, psi	62,900
Izod impact, ft-lb/in	17.4
Flammability, in/min (max.)	1.62
Water absorp., 24 hrs., %W (max)	+0.03
" " " " , %T (max)	+0.27
Rockwell M hardness	111
Specific gravity	1.91
30-Day Wet strength, flex., ult., psi	71,300
" " " " " , mod., x 10^{-6}	4.69
60 " " " ", , ult., psi	64,600
" " " " " , mod., x 10^{-6}	3.7
Flexural at 160°F, ult., psi	76,200
" " " mod., x 10^{-6}	3.7
" after accelerated service, ult., psi	68,500
" " " " " , mod., x 10^{-6}	3.21
Resin content, %w	28-33

The laminate used for the above tests contained 16 plies of glass fabric laminated parallel and was cured 5/25/330 at 25 psi.

Table 2. COMPARISON OF THE PHYSICAL PROPERTIES OF LAMINATES MADE WITH EPON 1001 CONTAINING 4 PHR DICYANDIAMIDE USING 181 GLASS FABRIC OF VARIOUS FINISHES

Finish	114	Improved Volan	136	Linde	RS49
Tensile, ult., psi	55,300	60,000	46,400	46,400	44,500
Flex., ult., psi	76,900	81,700	67,800	62,500	63,900
, tan. prop. limit	26,500	29,100	59,300	31,700	33,200
, mod., x 10^{-6}	3.72	3.5	3.3	2.7	3.5
After boiling 2 hours,					
flex., ult., psi	58,200	71,300	56,900	56,900	46,600
" , tan. prop.limit	24,800	33,100	46,000	35,200	34,700
" , mod., x 10^{-6}	3.6	3.5	3.5	3.0	2.5
After soaking 30 days					
flex., ult., psi	71,300	76,000	60,500	58,200	52,500
Compressive, ult., psi	70,200	57,400	62,400	57,400	55,800
Specific gravity	1.91	1.88	1.83	1.82	1.82
Rockwell hardness	111	116	114	110	106
% Resin	30	31	33	35	35
No. of plies	16	12	12	12	12

Laminates used for the above tests were cured 5/25/329 at 25 psi.

Table 3. PHYSICAL PROPERTIES OF LAMINATES MADE FROM 181 GLASS CLOTH IMPREGNATED WITH EPON X-12100 CONTAINING DICYANDIAMIDE AS CURING AGENT

Dicy, PHR	Laminate No.	Fabric Finish	Initial Cure a)	Final Cure b)	% Resin	Flexural, ult., psi Initial	After Boiling b)	After Soaking c)	After 1/2 Hr. at 300°F d)	After 200 Hrs. at 300°F d)	After 1/2 Hr. at 392°F d)
1	493	114	5/5/275	0/20/329	34	47,400	33,900	40,000	3,000		
2	494	"	"	"	37	69,500	38,300	47,000	8,800		
3	495	"	"	"	34	74,700	47,900	28,500	34,600		
3	534	"	"	"	29	74,700					
4	533	"	"	"	34	66,200					
4	527	"	"	"	32	75,800			33,900		
4	496	"	"	"	36	71,600			43,600		
6	541	"	"	"	33	61,700		31,200	37,700	57,200	61,900
8	542	"	"	"	32	69,600		29,100	39,700	48,200	61,100
2	484	"	0/10/275	0/20/329	33	70,500	39,000	31,300	11,200		
4	479	"	"	"	36	64,200	44,200	31,900	38,500	54,800	
4	485	"	"	"	32	63,600	46,300	30,800	41,400	55,500	
4	516	"	"	"	30	69,600		39,400	32,300		3,800
4	518	"	"	"	24	63,300		26,400	34,200		17,100
4	520	"	"	"	30	59,700					
4	522	"	"	"	33	66,800					
6	483	"	"	"	34	55,300	40,700	32,700	37,600	56,400	
3	537	"	10/0/275	0/20/329	33	71,300	48,400	46,600	23,600	57,700	36,200
4	500	"	"	0/30/329	35	65,200			43,700		
4	295	"	"	1/29/329	36	53,900			31,000	50,200	
4	552	"	"	2/28/329	33	61,900		36,200	34,300		34,700
4	553	"	"	5/25/329	36	38,000		18,000	19,300		26,700
4	498	"	5/5/239	0/20/329	38	59,500			36,500		
4	521	"	10/10/239	0/10/329	31	65,900					
4	528	"	0/10/239	0/20/239	26	60,800			38,400		
4	545	"	5/5/275	0/50/329	32	68,500		44,700	44,400	57,100	54,900
4	499	"	"	"	40	61,600	47,500	54,700	47,600		37,700

(Cont'd)

Table 3. PHYSICAL PROPERTIES OF LAMINATES MADE FROM 181 GLASS CLOTH IMPREGNATED WITH EPON X-12100 CONTAINING DICYANDIAMIDE AS CURING AGENT (CONT.)

Dicy. PHR	Laminate No.	Fabric Finish	Initial Cure[a]	Final Cure[b]	% Resin	Flexural, ult., psi					
						Initial	After Boiling[b]	After Soaking[c]	After 1/2 Hr. at 300°F[d]	After 200 Hrs. at 300°F[d]	After 1/2 Hr. at 392°F[d]
4	530	114	5/5/275	0/50/329	32	71,200					
4	474	"	2/8/275	0/20/329	36	59,200	41,700	32,900	35,100		
4	531	"	3/7/275	"	31	74,400					
4	532	"	7/3/275	"	37	69,000					
4	529[e]	BJY	5/5/275	0/20/329	33	69,500	54,600	58,500	47,400	64,600	58,300
4	554	"	"	"	32	62,600		53,200	25,900		33,300
4	517	"	"	"	32	66,200		51,700	39,700		29,000

a) In each group of 3 figures, the first designates the number of minutes at contact pressure, the second designates the number of minutes at 25 psi, and the third designates the temperature in degrees F.

b) Specimens were boiled 3 hours.

c) Specimens were soaked 30 days.

d) Specimens were tested at the temperature at which they were aged.

e) *Compressive strength* of Laminate 564, made same as No. 529, was 48,400 psi. No other compressive data are available.

Table 4. PROPERTIES OF LAMINATES CONTAINING LIQUID EPON RESINS CURED WITH DICYANDIAMIDE, USING 181-114 GLASS COTH

Laminate No.	EPON	Conc. Dicy., PHR	% Resin	Curing Conditions a)	Flexural, ult., psi. Initial	After Soaking b)	After 1/2 hr. at 300°F c)	After 200 hr. at 300°F c)	After 1/2 hr. at 392°F c)	Special Conditions
302	834	4	29	5/25/329	56,600					Minimum solvent d)
519	828	4	24	5/25/329	51,700	53,400	4,800		3,200	Ball milled e)
313	"	4	25	"	69,000		28,000	52,900		Minimum solvent d)
514	"	4	30	"	71,300	59,800	10,600		7,900	" "
475	"	4	39	5/25/329	65,500	52,700	11,000			
506	"	4	31	5/55/329	75,700	59,900	38,000		14,800	
505	"	4	31	8/22/329	66,800	56,300	9,400		7,000	
507	"	4	39	15/15/329	49,300	34,500	4,100		3,800	
546	"	6	26	5/25/329	74,200	40,900	12,200			
508	"	8	32	5/25/329	73,900	58,600	30,400		13,200	
509	"	8	32	5/55/329	73,100	63,300	44,000		14,000	
547	"	10	33	5/55/329	73,200	49,800	11,900			

a) In each group of 3 figures, the first designates the number of minutes at contact pressure, the second designates the number of minutes at 25 psi., the third designates the temperature in degrees F.

b) Specimens were soaked 30 days.

c) Specimens were tested at the temperature at which they were aged.

d) The only solvent used was that required to dissolve the dicyandiamide.

e) No solvent was used in the ball-milled mixture.

Table 5. STRENGTH OF LAMINATES MADE FROM 181-114 GLASS FABRIC IMPREGNATED WITH EPON 1001/RESIMENE P-97 MIXTURES

Resin Ratio EPON/ Phen.	Dicy., PHR	% Resin	Cure[a)]	Initial	Flexural, Ult., Psi		
					After boiling 3 hours	After soaking 30 days	At 300°F after 1/2 hour
90/10	4	35	2/28/329	66,200	50,800	67,100	5,800
90/10	4	34	5/25/329				
90/10	4	34	5/25/329	65,400	48,800	73,700	6,600
70/30	4	35	2/28/329	55,500			
70/30	4	32	2/8/275 0/20/329	64,100		56,800	4,000
70/30	4	35	2/28/275	55,500			
50/50	2	28	1/29/329	63,700			10,600
50/50	2	33	1/29/329	61,400		71,400	5,200
50/50	2	33	2/28/329	60,800		55,200	4,500

a) See text for explanation of this designation.

Table 6. STRENGTH OF LAMINATES MADE FROM 181-114 GLASS FABRIC IMPREGNATED WITH EPON 1001/PLYOPHEN 5015 MIXTURES

Resin Ratio EPON/ Phen.	Dicy., PHR	% Resin	Cure[a)]	Flexural, Ult., Psi			Compressive Ult., Psi
				Initial	After Soaking 30 days	At 300°F after 1/2 hour	
50/50	4	25	2/8/275 0/20/329	65,700	55,800	49,400	
"	"	26					
"	"	26	"	57,300	51,100	54,400	
"	"	26	5/5/275 0/20/329	65,100			51,600
70/30	"	24	2/8/275 0/20/329	59,200			
"	"	27	5/5/239 0/10/275 0/10/329	65,800			55,900
90/10	"	29	5/25/329	41,400			
"	"	31	5/5/275 0/20/329	66,600			54,600
0/100	"	25	2/28/275	52,700		47,100	

a) See text for explanation of this designation.

Table 7. PHYSICAL PROPERTIES OF VARIOUS EPON/GLASS CLOTH LAMINATES AT 300°F

Epon	Curing Agent	Flexural, Ult., Psi.			Special Conditions
		Room Temp.,	At 300°F		
			After 1/2 hr.	After 200 hrs.	
1001	Dicyandiamide	74,100	9,200	13,800	3 PHR curing agent
1001	"	71,500	8,100	12,000	6 " " "
1001	"	67,500	7,500	14,300	8 " " "
1001	"	77,000	10,100	13,800	Cured at 348°F
1001	"	76,900	12,100	12,000	Cured one hour
1001	"	78,900	8,600	15,900	Precured 8 minutes
1001	"	76,300	12,400	14,300	181-112
1001	"	66,800	5,900	17,000	181-112, powder lay-up
1004	"	71,800	5,400	9,000	
1001	Urea	66,200	4,700	6,500	
834	DMP-30[a)]	63,400	29,600		
"	DTA[b)]	65,100	11,300		
"	Phthalic anhydride	74,200	31,300		
848	DMP-30 tribenzoate[a)]	58,600	11,000	12,100	
"	" "	68,100	8,200	8,300	
"	" triacetate[a)]	62,100	11,300	11,400	
"	DMAPN[c)]	55,900	26,200	9,700[d)]	
"	Pyridine	63,800	19,500		
"	DMP-30[a)]	51,000	12,000		

a) DMP-30 = tri(dimethylaminomethyl)phenol.
b) DTA = diethylenetriamine.
c) DMAPN = dimethylaminopropionitrile.
d) At 392°F, after 1/2 hr. at 392°F, the flexural strength was 7,500 psi.

Laminates containing EPONS 1001 or 1004 were cured with 4 PHR of dicyandiamide for 30 minutes (including a 5-minute precure) at 329°F unless otherwise indicated. Glass cloth 181-114 was used, except as noted.

Table 8. PHYSICAL PROPERTIES OF LAMINATES MADE FROM 181-114 GLASS FABRIC AND EPON 828 RESIN CONTAINING VARIOUS FILLERS[c)]

Laminate No.	Filler	% Filler[a)]	% Resin[b)]	Flexural, ult., psi. Initial	Flexural, ult., psi. After Boiling
641	Blanc Fixc (barium sulfate)	5.2	27	56,600	34,500
642	"	12.7	24	55,900	36,600
646	HiSil (hydrated silicon dioxide)	6.2	32	55,500	36,900
640	Silene EF (precipitated calcium silicate)	7.0	36	53,500	33,800
638	Nepheline Syenite (diatomaceous earth)	6.0	31	47,500	33,800
639	"	15.8	30	44,300	26,800
634	Titanox (titanium dioxide)	4.9	25	55,900	36,900
635	"	12.7	26	57,000	40,700
643	Mapico Red No. 297 (iron oxide)	5.7	29	57,400	35,300
648	"	18.8	26	57,600	35,700
616	Witcarb Regular (precipitated calcium carbonate)	5.3	28	58,600	39,900
647	"	13.4	26	57,400	36,400
636	Powdered Slate	6.3	33	50,400	32,900
637	"	17.2	33	46,100	32,000
644	Zinc Sulfide	5.5	28	56,800	34,800
645	"	14.1	27	54,100	33,600
622	Witco No. 2 (china clay)	5.5	28	60,200	40,200
621	"	14.8	28	56,300	41,000

a) Percentage based on the total weight of the cured laminate.

b) Percentage of resin alone (exclusive of filler).

c) 5 PHR, DMP-30, added as the tri(2-ethylhexoate), was used as curing agent. The laminates were cured 2 minutes at contact pressure, followed by 28 minutes at 25 psi., 239°F.